

SEPARATIONS OF OLEFINS AND HETEROCYCLIC ORGANIC COMPOUNDS BASED ON REVERSIBLE COMPLEXATION REACTIONS.

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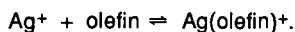
While numerous biological processes utilize membranes that contain transporting agents (carriers) to separate molecular and ionic permeates, the potential of synthetic membranes for separations in commercial processes has not been fully realized. In principal, the phenomenon of facilitated transport (FT) in membranes, which relies on the reversible formation of a permeate:carrier complex, can provide selective and efficient separations. Recently, membranes and thin films derived from ion exchange materials have received considerable attention with respect to their structural, physical and chemical properties. We report the facilitated transport of 1-hexene and 1,5-hexadiene between two decane phases separated by thin, hydrated membranes (ca. 25 μm). The flux of olefin across the membranes is enhanced by factors of several hundred when silver ions are exchanged for sodium ions.

Flux measurements were made using a two compartment cell arranged vertically and separated by the membrane which was held in place with o-rings and a clamp. The surface area of the membranes exposed to the solution was 1.8 cm^2 . Both compartments of the cell contained decane (20 mL) that had been saturated with water and were mechanically stirred to provide efficient mass transport to and from the membrane. The lower compartment contained either 1-hexene or 1,5-hexadiene (0.1 M). After the cell was assembled, aliquots (1 μL) of the solution were removed periodically with a syringe from the upper compartment and injected into a

gas chromatograph. The GC response for the olefins was monitored continuously by the injection of standards.

For membranes in the Na^+ -form, the flux of olefin across the membrane was quite low, but stable for over two days. Transport rates were much higher for the membranes in the Ag^+ -form. In both cases, plots of concentration of olefin in the upper compartment vs. time were linear. This indicates a constant flux of olefin across the membrane which can be readily calculated from the slopes: $J_{\text{Na}^+, \text{hexene}} = 2.4 \times 10^{-13}$, $J_{\text{Ag}^+, \text{hexene}} = 1.1 \times 10^{-10}$, $J_{\text{Na}^+, \text{hexadiene}} = 4.0 \times 10^{-13}$ and $J_{\text{Ag}^+, \text{hexadiene}} = 1.8 \times 10^{-10}$ (all J's in $\text{mol cm}^{-2} \text{sec}^{-1}$).

We attribute the enhanced olefin flux for the Ag^+ -form of the membrane to the reversible complexation of the olefins with silver ion:

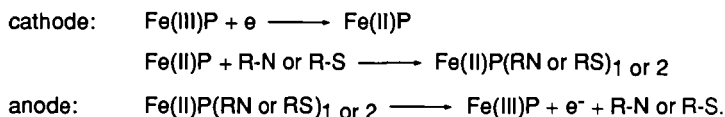


Formation constants for these complexes have been reported for 1-hexene ($K = 860 \text{ M}^{-1}$) and 1,5-hexadiene ($K = 1850 \text{ M}^{-1}$) in 1 M aqueous AgNO_3 . Assuming that the enhanced fluxes are due to facilitated transport associated with the mobility of the Ag(olefin)^+ complex, facilitation factors, F , can be calculated as the ratio of the olefin flux for the Ag^+ -form to the flux for the Na^+ -form. From the fluxes calculated above, $F_{\text{hexene}} = 460$ and $F_{\text{hexadiene}} = 450$.

Synthetic fuels derived from coal liquids, tar sands or oil shale contain a wide variety of nonvolatile chemical compounds containing nitrogen and sulfur. Many of these compounds display mutagenic or carcinogenic activity. Therefore, these classes of compounds are undesirable pollutants which must be removed from fuels and other related hydrocarbon products.

We are exploring a novel process for the selective removal of organic nitrogen and sulfur compounds (R-N and R-S) from hydrocarbon phases. The process is based on electrochemically modulated chemical complexation. The complexing agents are

water-soluble derivatives of Fe metalloporphyrins. A porphyrin (P) is a tetradentate macrocyclic ligand. Metalloporphyrins have numerous biological functions including the transport of oxygen. The metal ions in metalloporphyrins bind other molecules (ligands) in addition to the porphyrin itself. These bonds are perpendicular to the plane of the porphyrin so the bound molecules are referred to as axial ligands. Reversible reactions between metalloporphyrins and organic compounds containing nitrogen and sulfur are the basis for this separation process. In general, these complexation reactions have greater equilibrium constants when the metals are in the +2 oxidation state as opposed to the +3 state. Interconversion of the Fe(III) and Fe(II) states in metalloporphyrins is a kinetically facile process at metal electrodes. By applying relatively mild potentials, we can achieve the cyclical process:



The reactions described above can be incorporated into a staged electrochemical separation process. Results for the removal of isoquinoline and pentamethylene sulfide from iso-octane and the subsequent concentration of these compounds in a second (waste) hydrocarbon phase will be presented.